

PREPARATION AND PROPERTIES CHARACTERIZATION OF
 $\text{P}_2\text{O}_5\text{-KNO}_3\text{-K}_2\text{O}$ GLASS

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ABSTRACT

A series of glass based on $50\text{P}_2\text{O}_5\text{-xKNO}_3\text{-(50-x) K}_2\text{O}$ system where $0 < x \leq 50$ mol % has successfully been prepared using melt-quenched technique. The glass crystallinity has been confirmed using X-Ray Diffraction (XRD) analysis while the microhardness is measured using Vickers indenter. It is found that the microhardness is in the range of 146 Hv to 178 Hv as the mol % of KNO_3 content increases. The glass density, which is measured using the digital balance, is found to be in the range of 2.3820 gcm^{-3} to 2.4232 gcm^{-3} as the mol % of KNO_3 content increases. The molecular bond structures and the characteristic of H-OH molecular vibrations in the glass are investigated using Infrared absorption spectrometer in the range of 370 cm^{-1} to 3800 cm^{-1} . It has been found that the nitrogen incorporated into the glass network by replacing the bridging oxygen. It is also found out that the increase in the mol % of KNO_3 content will cause the corrosion rate of the glass in pH 1, pH 3, pH 5 and pH 7 solutions to fall from $5.83 \times 10^{-3} \text{ gcm}^{-2}\text{min}^{-1}$ to $0.25 \times 10^{-3} \text{ gcm}^{-2}\text{min}^{-1}$. All of the solutions experience the increase in pH value after the 20 minutes corrosion test.

ABSTRAK

Satu siri kaca berasaskan sistem $50\text{P}_2\text{O}_5\text{-xKNO}_3\text{-(50-x) K}_2\text{O}$ dengan $0 < x \leq 50$ mol % telah berjaya disediakan melalui kaedah pelindapan leburan. Kehabluran kaca telah dipastikan menggunakan analisis Pembelauan Sinar-X (XRD) manakala kekerasan mikro telah diukur menggunakan penusuk Vickers. Didapati bahawa julat kekerasan mikro adalah dari 146 Hv hingga 178 Hv dengan pertambahan kandungan mol % KNO_3 . Ketumpatan kaca pula telah disukat menggunakan penimbang digital dan didapati berada dalam julat 2.3820 gcm^{-3} hingga 2.4232 gcm^{-3} dengan pertambahan kandungan mol % KNO_3 . Struktur ikatan molekul dan sifat getaran molekul H-OH dalam kaca dikaji menggunakan spectrometer serapan infra merah dalam julat 370 cm^{-1} hingga 3800 cm^{-1} . Didapati bahawa nitrogen masuk kedalam rangkaian kaca dengan menggantikan titian oksigen. Didapati juga bahawa pertambahan kandungan mol % KNO_3 akan menyebabkan kadar kakisan kaca dalam larutan pH 1, pH 3, pH 5 dan pH 7 menurun dari $5.83 \times 10^{-3} \text{ gcm}^{-2}\text{min}^{-1}$ hingga $0.25 \times 10^{-3} \text{ gcm}^{-2}\text{min}^{-1}$. Kesemua larutan tersebut mengalami kenaikan nilai pH setelah 20 minit ujian kakisan dijalankan.

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LIST OF SYMBOLS

| | | |
|------------|---|---|
| A | - | Surface area |
| DR | - | Dissolution Rate |
| F | - | Load (Force) |
| f | - | Force constant of molecule bonding |
| H | - | Ratio of load and surface area |
| h | - | Height |
| l | - | Length |
| l_1, l_2 | - | Diagonal length |
| m | - | Order of the diffraction peak |
| m_1, m_2 | - | Mass of atoms in molecule |
| n | - | Number of bridging oxygen per tetrahedral |
| O_B | - | Bridging oxygen |
| O_T | - | Terminal oxygen (Non-bridging oxygen) |
| Q^n | - | Phosphate tetrahedral group |
| R | - | Ratio of M_2O to P_2O_5 |
| S_A | - | Exposed area |
| T | - | Transmission |
| T_c | - | Crystallization Temperature |
| T_g | - | Glass Transformation Temperature |
| t | - | Time |
| W | - | Sample weight before immersion |
| W_a | - | Glass weight in air |
| W_L | - | Glass weight in liquid |
| W_o | - | Sample weight after immersion |
| w | - | Wide |
| ν | - | Vibration frequency |
| δ | - | Error |

| | | |
|-----------|---|---------------------------------|
| θ | - | Angle |
| λ | - | Wavelength |
| μ | - | Reduced mass of molecule system |
| ρ_g | - | Density of glass |
| ρ_L | - | Density of liquid |

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

In the 1950s, interest in amorphous alkali phosphate was stimulated by their use in a variety of industrial applications, including sequestering agents for hard water treatments and dispersants for clay processing and pigment manufacturing. By studying such materials, Van Wazer established the foundations for much of present understanding about the nature of phosphate glasses [1].

Phosphate glasses are technologically important materials due to their low melting point and relatively high thermal expansion coefficients, which suit them as a potential candidate for technological application, such as in medical use on solid state electrolytes [2]. Phosphate glass also possesses low glass transition temperature and low softening temperature which are increasing interest for many applications such as glass to metal seals, thick film paste, the molding of optical elements and low temperature enamels for metals [3,4].

Some other characteristics such as chemical durability, density, IR spectra and hardness of phosphate glass have also been investigated and attracted many interests for immobilizing some level nuclear wastes, many of which contain one or more alkali oxides [5, 6].

Phosphate glasses can also be a good candidate for fertilizer due to their fast dissolution in aqueous solution [7, 8]. The remarkable bioactivity and compatibility of the phosphate glasses also attracted the attention of scientists in the fields of biomedical research to use them as medical materials and potential controlled release carriers of medicine [9-12].

The enormous applications of these glasses are mainly due to the capability to change their chemical durability character. Day and Reidmeyer produced nitrogen-containing phosphate glasses in the early 1980s by treating the melt in anhydrous ammonia gas or adding nitrogen compounds to the melt [13]. They found that doubly and triply coordinated nitrogen ions replace the bridging and non-bridging oxygen ions in the PO_4 tetrahedral.

1.2 Problem Statement

Although there have been many investigation on phosphate based glass, the effect of nitrogen on their properties such as hardness, glass transition temperature, Young's modulus, viscosity and others were not systematically being reported. It is therefore the aims of this study to prepare and to investigate the physical, mechanical, optical, and the chemical durability of $50\text{P}_2\text{O}_5\text{-xKNO}_3\text{-(50-x)K}_2\text{O}$ glass where $0 \leq x \leq 50$ mol % will be presented. This study is deemed useful for future researchers in order to wider understanding and application of phosphate glass. All the results will be discussed with respective to the composition.

1.3 Scope of the Study

This research study only covers the preparation of multi component phosphate glass in $50\text{P}_2\text{O}_5\text{-xKNO}_3\text{-(50-x)K}_2\text{O}$ ternary system which $0 \leq x \leq 50$ mol % via melt quenching technique and characterization of some properties of the glass. The characterization of the glass is focusing on:

- i. Density based on the structure changers.
- ii. Hardness based on its composition.
- iii. Absorption infrared spectroscopy of glass molecule.
- iv. Chemical durability based on its compositions in the range between pH 1 to pH 7 conditions.

1.4 Objectives of the Study

The objectives of the study are as follows:

- i. To identify the glass formation range based on $50\text{P}_2\text{O}_5\text{-xKNO}_3\text{-(50-x)K}_2\text{O}$ system which $0 \leq x \leq 50$ mol %.
- ii. To determine the density and correlate with the changing of the glass structure.
- iii. To correlate the composition and the hardness of the glass.
- iv. To analyze the infrared absorption spectroscopy of the glass.
- v. To observe the effect of composition to chemical durability of the glass and to evaluate the chemical durability of the glass in pH 1, pH 3, pH 5 and pH 7 conditions.
- vi. To determine the pH changes of solutions in order to understand the behavior of the glass corrosion.
- vii. To observe the effect of nitrogen to the properties of glass.

1.5 Choice of the System

In this study, phosphate glass based on $50\text{P}_2\text{O}_5\text{-xKNO}_3\text{-(50-x)K}_2\text{O}$ system was chosen. This is important especially in view of the effect of nitrogen (with the nitrate as a source) in alkaline phosphate glasses. The study was done to the glass sample that was prepared in the range of $0 \leq x \leq 50$ where x is mol %.

P_2O_5 was chosen as a host because of its low melting point, wide glass formation region and shows good chemical properties [14, 15]. KNO_3 was selected as the source of nitrogen since it is the simply method to add nitrogen into the glass.

In this study, K_2O was used as modifier since it is very active chemically [16]. It is also useful from the lowest temperature range to the highest [17]. K_2O is very similar to Na_2O in its action in glasses. However, there are the couple minor differences. In the first place, potassium improves the gloss of the glass relative to soda. Second, in aluminosilicate formulations, the viscosity at given temperature of a potassium system is higher than of an equivalent soda system.

1.6 Thesis Plan

This thesis is divided into five chapters. The first chapter is a brief of introduction. In second chapter, reviews of background and current knowledge on phosphate glass are presented. It will include the general theory on glassy state, phosphate glass fundamental structure, a special survey on the phosphate glass formation region, density, Vickers microhardness, infrared absorption spectroscopy, and chemical durability.

In third chapter, the experimental and theoretical aspects that have been employed in this research will be described in detail. This will include the preparation of the glass, X-Ray Diffraction (XRD), observation of nitrogen content by Energy Dispersive Analysis by X-Ray (EDAX), evaluation of density, determination of hardness and infrared absorption spectroscopy. The end of the chapter will discuss the experimental works on the observation of the glass chemical durability behavior.

The experimental results and findings with discussions will be presented in fourth chapter. This chapter will give a special attention on the glass properties.

Finally, in fifth chapter, some conclusions that may be extracted from this research are presented. This would also include some suggestions for the future studies and investigations.

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